Uranium vanadium mineralization in Mississippian aged paleokarst, northern Bighorn Basin, Montana and Wyoming indicates a hydrothermal Permian Phosphoria Formation source of metals including REE and Tl

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GSA Annual Meeting in Denver, Colorado, USA – 2016

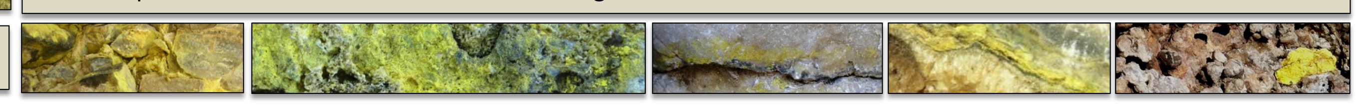
ABSTRACT:

The origin of V, REE and other metals in the Permian Phosphoria Formation have been speculated and studied by numerous scientists. The exceptionally high concentrations of metals have been interpreted to be the result of a continuous strong upwelling marine environment reflecting fundamental transitions from anoxic to oxic marine conditions. Past productive U and V deposits hosted in Mississippian aged paleokarst of the northern Bighorn Basin, MT and WY have a close association with hydrocarbons and contain anomalous high concentrations of many metals that are found in similar concentrations in the Permian Phosphoria Formation. Original Phosphoria Formation sourced hydrocarbon accumulation in the Bighorn Basin was in stratigraphic traps created primarily by up dip facies change, pinch out and truncation of the reservoir carbonates, and by uneven Permo-Triassic Goose Egg Formation truncation of underlying Tensleep Sandstone. These stratigraphic traps were later released because of fracturing and faulting associated with Laramide folding and migrated into older Paleozoic reservoir rocks. Mineralizing fluids are interpreted to have migrated into collapse paleokarst by episodic tectonic brecciation related to hydrothermal activity due to crustal shortening during the Laramide orogeny. Isotopically depleted fluids with $\delta^{18}O$ compositions between -24.8 and -11.99‰ VPDB indicate fluids with elevated temperatures cemented the breccia. Groups of minerals from different mines have similar $^{87}Sr/^{86}Sr$ compositions while within each mine site the $^{87}Sr/^{86}Sr$ composition of minerals vary. Some of the samples show enrichment of REE plus Y. Thallium (Tl) is found in anomalous concentrations in both the Phosphoria Formation and in all the mineralized samples from the U-V deposits (10-490 ppm) of this study. Tl is not commonly concentrated in many rock types and Tl minerals are rare. Tl has been shown to be associated with hydrothermal sourced fluids in sediment hosted gold deposits. The average crustal abundance of Tl is 0.75 ppm. Bighorn Basin oilfield brines likely provided a transporting fluid and a source of metals for ore and gangue minerals in the U-V mining districts in the northern Bighorn Basin.

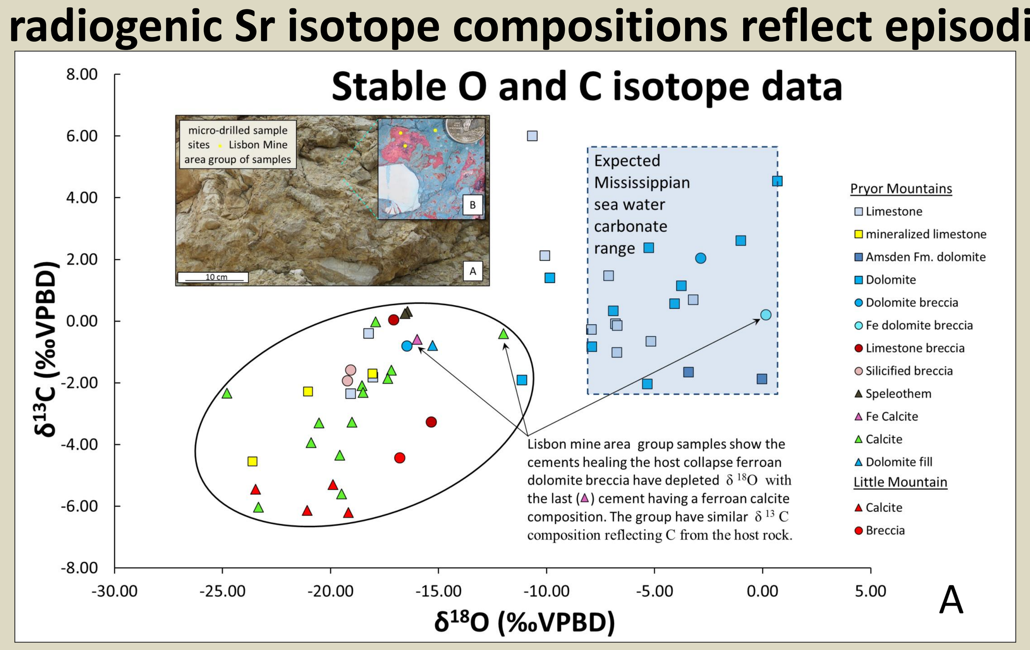
Top: View of Gypsum Creek anticline from Lisbon Mine, Pryor Mountains, Montana. **Right:** Typical yellow U-V mineral occurrences from both mining districts.

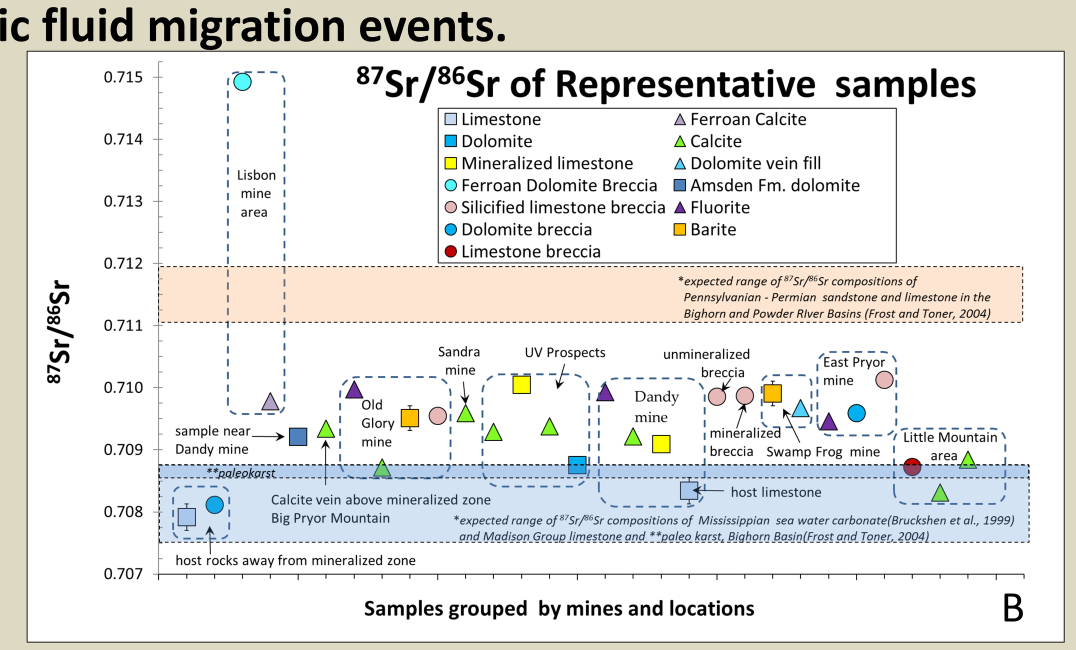
Several theories exist for the origin of the MT/WY U-V deposits:

1) One theory proposed that U-bearing meteoric water leached U from tuffaceous material or ash that once covered the region in Tertiary time and deposited it in preexisting karst solution cavities (**Top down theory**).
2) A structurally controlled, ascending hydrothermal fluid interpretation based on identification of davidite, a high temperature U-REE oxide mineral and associated fluorite was proposed by some workers. A dozen years after mining ceased, the U.S. Department of Energy identified a N-S trending, 30 km long magnetic high anomaly located to the SW of the Big Pryor block. An inferred intrusion, a potential source of the magnetic anomaly, could provide ascending hydrothermal fluids and a heat source for the MT/WY deposits (**Bottom up theory).**
3) The abundance of caves, especially in the Little Mountain Mining District, supports a hypogenic karst origin with groundwater mixing. Support for this model is the nearby Kane Cave system in the Little Sheep Mountain anticline, WY. The Lower Kane cave, hosted in Madison limestone (Mm) in the core of the anticline, is actively forming by hypogenic sulfuric acid speleogenesis (SAS). (**Combination theory)**
4) Potential V sources are the Permian Park City Formation (Phosphoria Formation equivalent in MT) or V-rich Phosphoria Formation sourced oil from the Bighorn Basin.



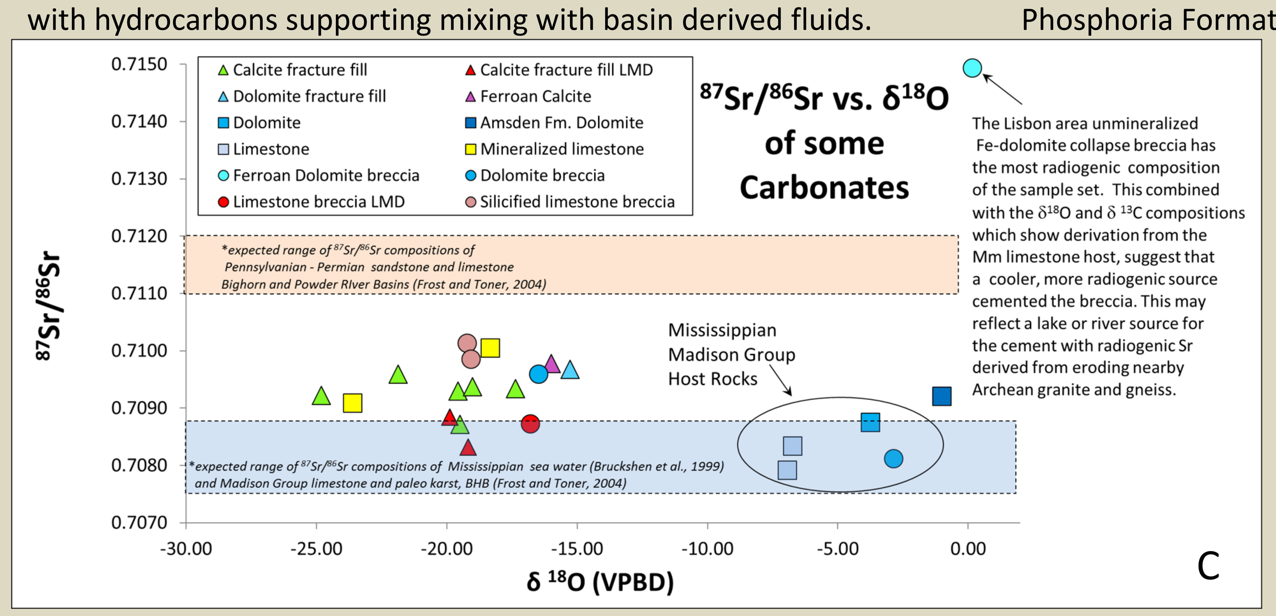
C and O stable isotope results support episodic hydrothermal fluids precipitating cements and radiogenic Sr isotope compositions reflect episodic fluid migration events.





(A) The $\delta^{18}O$ and $\delta^{13}C$ compositions distinguish Mississippian age host rock from the most depleted values of this study that plot in the oval. The depleted $\delta^{13}C$ of may reflect carbon derived from contamination with hydrocarbons supporting mixing with basin derived fluids.

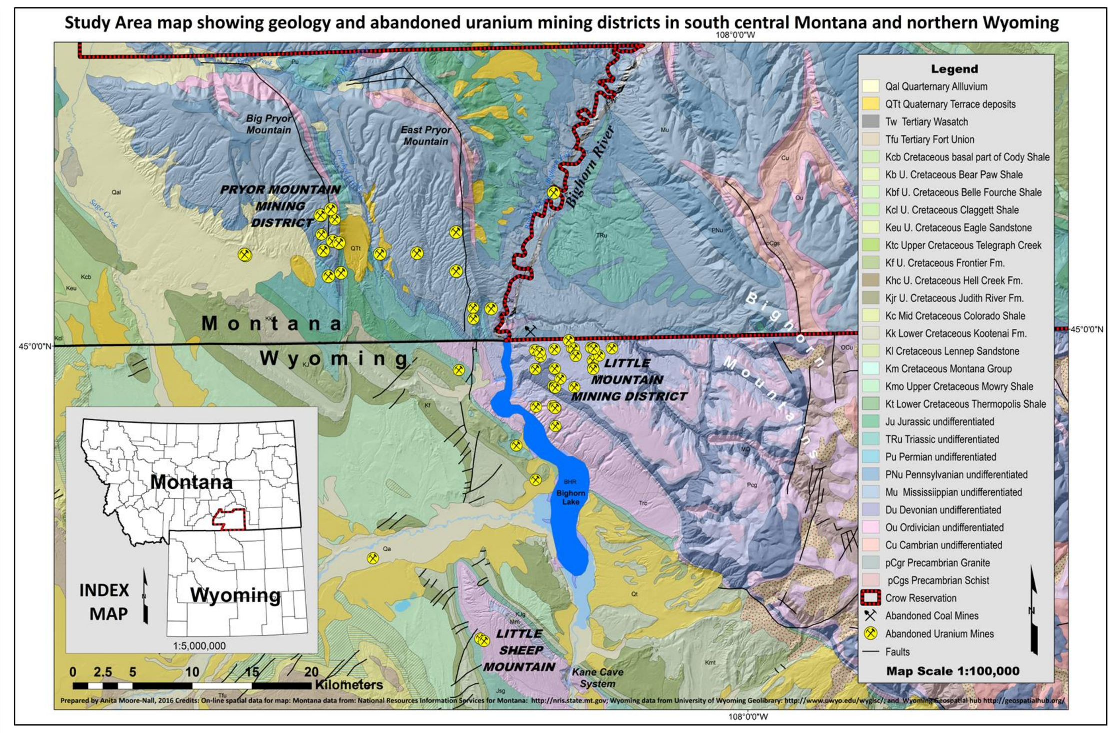
(B) Variable $^{87}Sr/^{86}Sr$ composition indicates the precipitation of minerals did not all form simultaneously from the same fluid. The LMD samples reflect a Mm Sr source while the PMD reflect Pennsylvanian-Permian hosted fluids likely with Phosphoria Formation sourced hydrocarbons mixing with the Madison host rock.



(C) Data analyzed for both O & Sr isotopes show mineralized samples and vein fill material have the most depleted $\delta^{18}O$ composition. Most are more radiogenic than the Mm host rocks that are enclosed by the oval. The Little Mountain samples reflect a Madison Group limestone and paleokarst source.

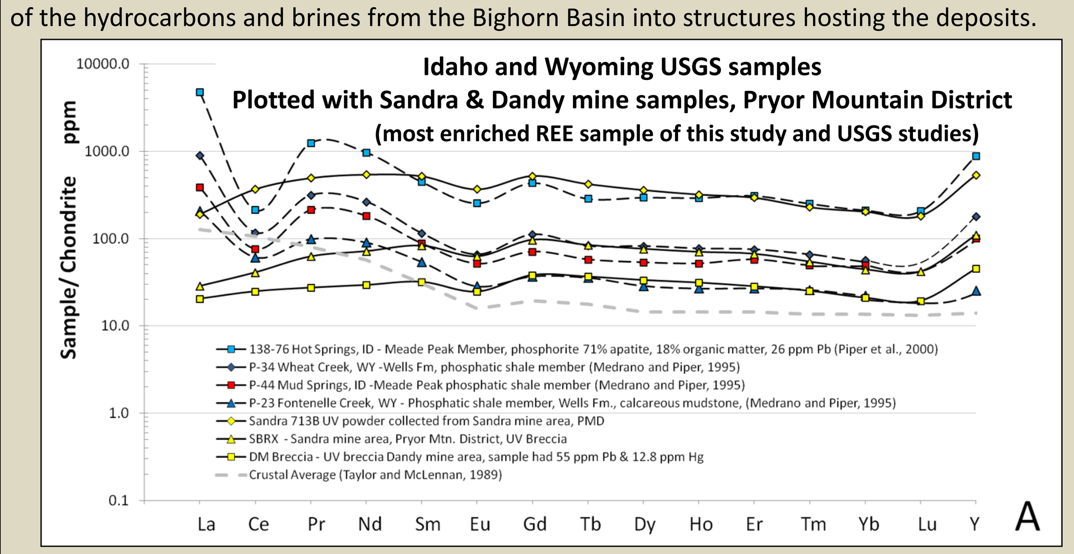
U-V mineralized hematite and limonite-stained hydrothermal breccia cuts across Mm paleokarst collapse breccia near the Sandra Mine, Pryor Mountains, MT. A 20 cm arrow for scale. Mineralization is in vugs and along fractures.

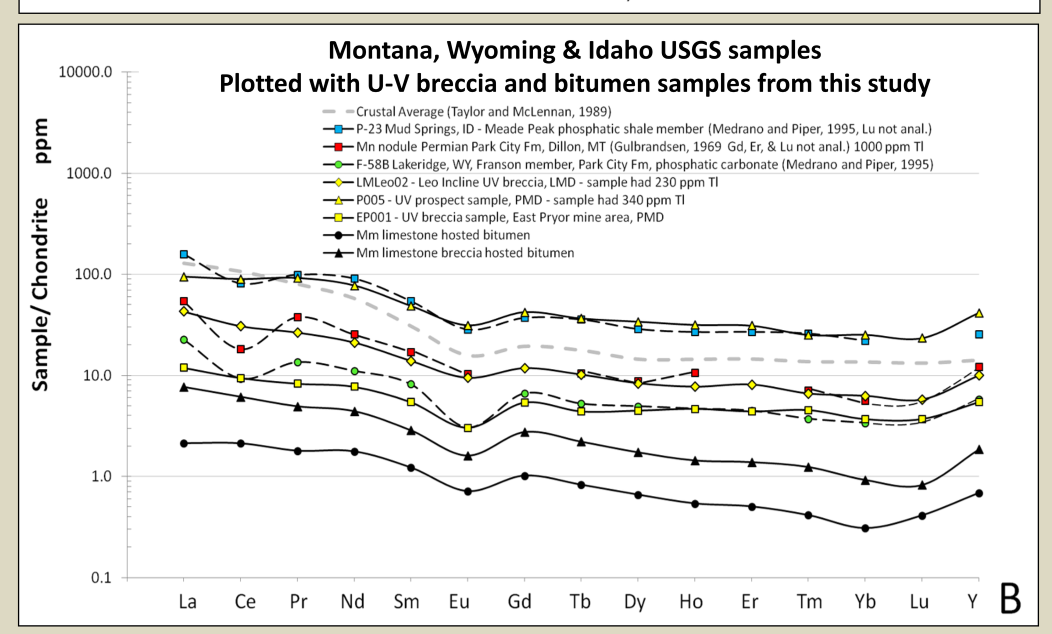
Study Area map showing geology and abandoned uranium mining districts in south central Montana and northern Wyoming



REE RESULTS:

The oil in the Bighorn Basin has been determined to be mainly sourced by dark organic-rich and phosphatic, fine grained sediments of the Permian Phosphoria Formation [Stone, 1967]. The bitumen that is included in the graphs below is likely a product of that migration. Data from several studies of the Phosphoria Formation in ID, WY and MT was examined. Spidergram plots of REE plus Y normalized to CI using the values of Anders and Grevesse, 1989, were produced from some of the data which had similar concentrations with some data from this study. The samples in our study lack the distinctive negative Ce anomaly characteristic of seawater though have similar HREE and Y patterns to the USGS rock sample REE patterns. The patterns from this study likely represent the fractionation of the REE as a group with the maturation and migration of the hydrocarbons and brines from the Phosphoria Formation into structures hosting the deposits.





OTHER METALS:

Metals detected in this study that have similar high concentrations to Phosphoria Fm. samples from USGS studies are highlighted in red in the table below. Tl was anomalously high in several 10's of ppm, some higher values (130 – 1000 ppm) have been documented. Unmineralized host rocks, quartz, fluorite, barite and calcite were not analyzed for many of these elements and are not included in the table. W and Re (highlighted in blue) were not analyzed in the USGS studies. W was anomalously high in samples from this study. Re was detected in bitumen analyzed for REE by Aqua Regia and ICP-AES/ICP-MS in a 51-element package. Other samples were analyzed for REE by by Lithium Borate Fusion and ICP-MS in a 30-element package which did not include Re. V and other metals in the bitumen support a Phosphoria Formation hydrothermal origin for fluids precipitating minerals or as inclusions in minerals present in these deposits.

District	Sample	As	Ba	Hg	Mo	Ni	Pb	Re	Se	Sr	Tl	U	V	W	Zn
locality	*avg. crustal abundance (ppm)	.8-1.5	150-500	0.067	0.8-1.5	44-156	~5-17	0.0004	0.05	230-350	0.2-0.8	0.5-3	107-271	0.7-2	71-83
PMD	FS131A UV breccia	262	1230	2.84	53	<1	<2	na	na	257	180	86800	18900	94	16
PMD	Swamp Frog UV breccia	556	1320	0.396	791	11	<2	na	na	192.5	340	6100	4160	81	44
PMD	SBRX Sandra mine area UV breccia	49	5460	0.333	11	38	7	na	na	182.5	10	2600	1950	71	136
PMD	MarieMine UV breccia	87	533	1.715	319	15	<2	na	na	62.5	30	2100	6740	40	57
PMD	Perc Group UV breccia	329	5170	1.21	52	19	51	na	na	227	170	20700	6700	30	95
PMD	OGM04 Old Glory mine UV breccia	1295	2310	0.354	152	2	13	na	na	1355	100	10600	4410	105	26
PMD	P005 Prospect UV breccia	1080	1305	1.255	386	80	18	na	na	980	340	9000	6010	19	165
PMD	Sandra713B UV powder	99	6550	1.485	29	167	44	na	na	188.5	20	21400	8730	24	804
PMD	D2001 Dandy mine UV breccia	87	79.5	6.32	9	2	35	na	na	132.5	50	17700	6310	16	849
PMD	DandyMSPF Stock pile UV breccia	30	39.6	3.4	4	21	8	na	na	128	10	3000	3320	12	76
PMD	DandyMBr UV breccia	130	61.3	12.8	28	102	55	na	na	147.5	20	28100	10500	26	1110
PMD	OGM UV blk UV breccia	46	1530	na	21	<1	2	na	na	110	50	4900	1240	107	7
PMD	DandyMSP UV breccia	94	2470	na	20	<1	35	na	na	513	490	8600	2220	382	9
PMD	EP001 E. UV breccia	50	27.6	na	2	63	11	na	na	84.7	10	907	25	6	143
LMD	LMLeo02 UV breccia	726	255	0.179	137	517	57	na	na	401	230	16000	10300	11	2230
LMD	LMLeoIncline UV breccia	116	183	na	98	191	28	na	na	168.5	20	>1000	4330	13	970
LMD	LMLisbonBX UV breccia	212	140	na	93	122	4	na	na	151.5	10	1300	1850	12	569
LMD	LMLisbon UV breccia	89	42.6	0.197	25	421	146	na	na	261	30	31100	8520	11	1300
LSM	Mm hosted bitumen	0.2	10	0.01	1.63	14.1	0.9	0.028	3.2	76.4	0.02	6.8	73	8.63	5
LSM	Mm breccia hosted bitumen	<0.1	20	<0.01	0.12	1.5	0.5	0.001	0.5	156	<0.02	4.04	7	2.38	2

*McLennan, S. M. (2001) PMD= Pryor Mountain District LMD = Little Mountain District LSM = Little Sheep Mountain na = not analyzed

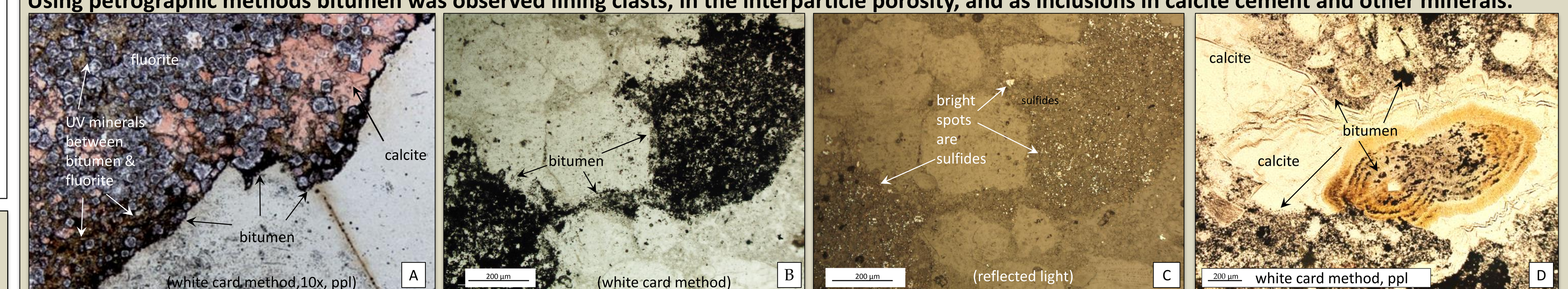
MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION:

Samples were chosen to test theories for the origin of these deposits. Rock samples included breccia clasts and matrix samples, altered and unaltered host rock, generations of cements from veins, and mineralized samples from dumps and outcrops. Bitumen was collected from fractures in Mississippian age Madison limestone and paleokarst collapse breccia to compare the chemical composition with our samples to see if there may be an association with the oil and brines from the Bighorn Basin and to test the hydrothermal theory.

Work performed to complete analyses in the study areas included: standard petrography, scanning electron microscopy (SEM) utilizing energy dispersive x-ray spectrometry (EDS) and backscatter electron imaging (BSE), cathodoluminescence (CL), powder x-ray diffraction (XRD) spectroscopy, stable C, O, and radiogenic Sr isotopic analysis. Commercial assays were performed by an Australian Laboratory Services (ALS) Global branch out of Reno, Nevada.

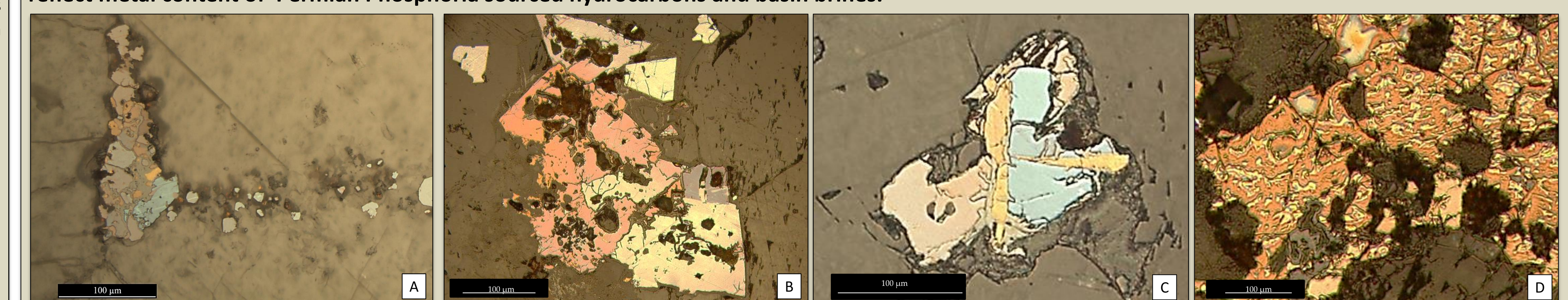
DISCUSSION AND RESULTS:

Using petrographic methods bitumen was observed lining clasts, in the interparticle porosity, and as inclusions in calcite cement and other minerals.



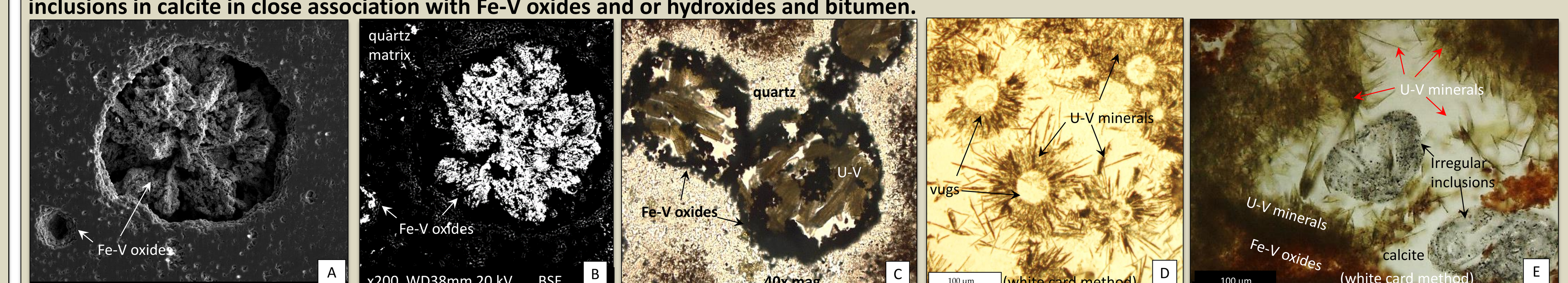
(A) Bitumen lining clast of silicified limestone. Red stained calcite fills in porosity of oolites metasomatically replaced by fluorite, Dandy mine, PMD, ppl, white card method (Folk, 1987) **(B)** Bitumen filled in porosity of E. Pryor mine breccia, ppl, white card method **(C)** Sulfides appear bright in reflected light view of B. **(D)** Calcite filling in fracture with bitumen inclusion "bleeding" out in concentric rings, Dandy mine, PMD, ppl, white card method.

Isotropic Fe-Sulfides present in interparticle porosity and along fractures shown in plane polarized reflected light with different colors and textures likely reflect metal content of Permian Phosphoria sourced hydrocarbons and basin brines.



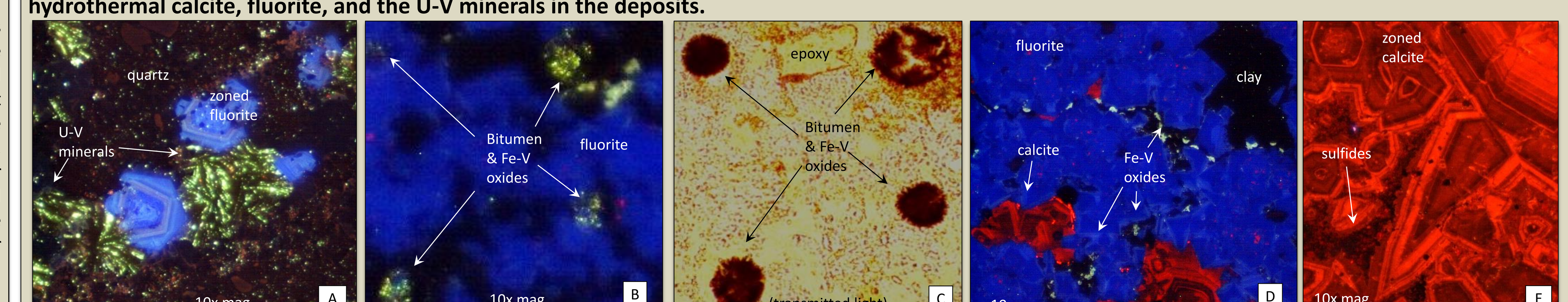
(A) Four isotropic minerals are shown in this view, blue may be Ni-bearing pyrite and pinkish brown may be bornite Cu_5FeS_4, E. Pryor mine **(B)** Three different minerals intergrown together, E. Pryor mine **(C)** Three different minerals occur together, Marie mine **(D)** Exsolution texture of two minerals, E. Pryor mine, the yellow mineral may be pyrite.

Fe-V oxides are present in vugs of silicified tectonic hydrothermal breccia that likely formed after hydrocarbons or volatiles were released or dissolved out during episodic fluid migration. U-V minerals formed inside these vugs in the PMD. U-V minerals formed around spherical vugs or irregular inclusions in calcite in close association with Fe-V oxides and or hydroxides and bitumen.



(A) Spherical vugs in quartz matrix of THB, Old Glory mine, PMD, SEI, 200x mag. **(B)** BSE of A, microscopic Fe-V oxides visible in large vug and lining smaller vug. **(C)** Tyuyamunite or metatyuyamunite crystals in Fe-V oxide lined, bleached circular vugs **(D)** Tyuyamunite or metatyuyamunite crystals radiating out from circular vugs after hydrocarbons or volatiles in fracture appear dark due to Ir coating on slide used for SEM work, Leo Incline area, Little Mountain Mining District, ppl, white card method **(E)** Tyuyamunite or metatyuyamunite crystals nucleated (?) on Fe-V oxides or hydroxides in fracture. Some appear to have grown into irregular inclusion that has some black bitumen preserved inside.

Cathodoluminescence revealed the episodic nature of calcite and fluorite and highlighted U-V minerals and Fe-V oxides present along fractures and interparticle porosity. Permian Phosphoria sourced hydrocarbons likely provided a source of V and REE which contributed to the luminescence in hydrothermal calcite, fluorite, and the U-V minerals in the deposits.



(A) U-V minerals luminesce bright green with hexaoctahedral blue and lilac zoned fluorite in vug of a silicified breccia from the Old Glory mine. **(B)** Fluorite and bitumen with Fe-V oxides and bitumen spheres, Marie mine, PMD **(C)** Transmitted light view of B. **(D)** Zoned calcite with bitumen and Fe-V oxides filling in the porosity, Lisbon mine, LMD. **(E)** Concentric zoned calcite from the East Pryor mine area, darker zones are Fe-rich zones and marcasite or pyrite fills in porosity between crystals.

ACKNOWLEDGMENTS: We thank employees of the Bureau of Land Management, Cody, Wyoming, who granted permission for the work in the Little Mountain area; Wyoming High-Precision Isotope Laboratory group: Kens Sims, Erin H.W. Phillips and Sean Scott for assistance and guidance with Sr separation; Adina Paytan, Institute of Marine Sciences, University of California, Santa Cruz, CA for Sr separation from barite samples and Nancy Equall and Laura Kellerman from the Image and Chemical Analysis Laboratory at Montana Sate University for assistance and guidance with instrumentation at the lab. Funding for research: ZERT II (Zero Emmissions Research) DOE Award #: DE-FE0000397; Alfred P. Sloan Graduate Scholarship Programs—Sloan Indigenous Graduate Partnership; Montana State University Dennis and Phyllis Washington Foundation Native American Graduate Fellow; HOPA Mountain Program.

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